Mineral Assemblages at IODP Sites U1387 and U1389, Gulf of Cadiz: Definition by Principal Component Analysis and Interpretation of Their Geologic Significance

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TABLE OF CONTENTS

Abstract

The Gulf of Cadiz and the West Iberian margin were the location where Expedition 339 of the Integrated Ocean Drilling Program (IODP) collected sediment cores to better understand the Mediterranean Outflow Water (MOW) and its history. Sediment from Sites U1387 and U1389 was analyzed by X-ray diffraction (XRD) method aboard the JOIDES Resolution to determine the bulk mineralogy at the two sites. In this study, shipboard data were processed using Paleontological Statistics (PAST) software to identify mineral assemblages using principal components analysis. The mineral assemblages were defined by covarying minerals, and were used to determine sediment provenance. At Site U1387, the three most important principal components defined five mineral assemblages that consisted of plagioclase, dolomite, kaolinite, K-feldspar, augite, aragonite and chlorite. At Site U1389, the three most important principal components defined six mineral assemblages made up of plagioclase, dolomite, chlorite, and aragonite. Principal Component 2 at Site U1387 and Principal Component 1 and 3 at Site U1389 are indicative of a relationship between marine biogenic vs. terrigenous detrital sediment supply, and the other principal components identify various assemblages of detrital terrigenous minerals. The results generally identified a local provenance from the Guadiana and Guadalquivir Rivers, with erosion of exposed beaches and cliffs as other possible sources of sediment supply. This supports the

conclusion that Gulf of Cadiz sediments have been supplied from a variety of nearby areas, with transport and deposition influenced by many environmental and geological influences.

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college, and life in general. If it were not for my family, friends, and loved ones I would not be where I am today.

Introduction

Expedition 339 of the Integrated Ocean Drilling Program (IODP) was focused on studying the history of Mediterranean Outflow Water (MOW), and how it affects the climate and circulation of the North Atlantic Ocean. This expedition allowed scientists to study and link paleoceanographic, climatic, and sea level changes from the Messinian to the present day. This linkage proved the importance of ocean gateways in regional and global ocean circulation and climate change (Hernandez-Molina et al., 2013; Expedition 339 Scientists, 2013a).

Seven sites were drilled during Expedition 339, five in the Gulf of Cadiz and two sites off the West Iberian margin. Included in those seven were Sites U1387 and U1389, which were examined in this study. Most sites were located to examine the contourite depositional system (CDS) (Figure 1) generated by the MOW influence in the Gulf of Cadiz and on the West Iberian margin. The CDS is a direct result of MOW and it provides a sedimentary record that allows scientists to link past environmental changes to paleocirculation patterns (Expedition 339 Scientists, 2013a). Site U1387 is located on the southern Iberian margin near the Portuguese city of Faro (Figure 2). This site is at the eastern end of the Faro Drift, and the core retrieved recovered middle-slope contourite deposits.

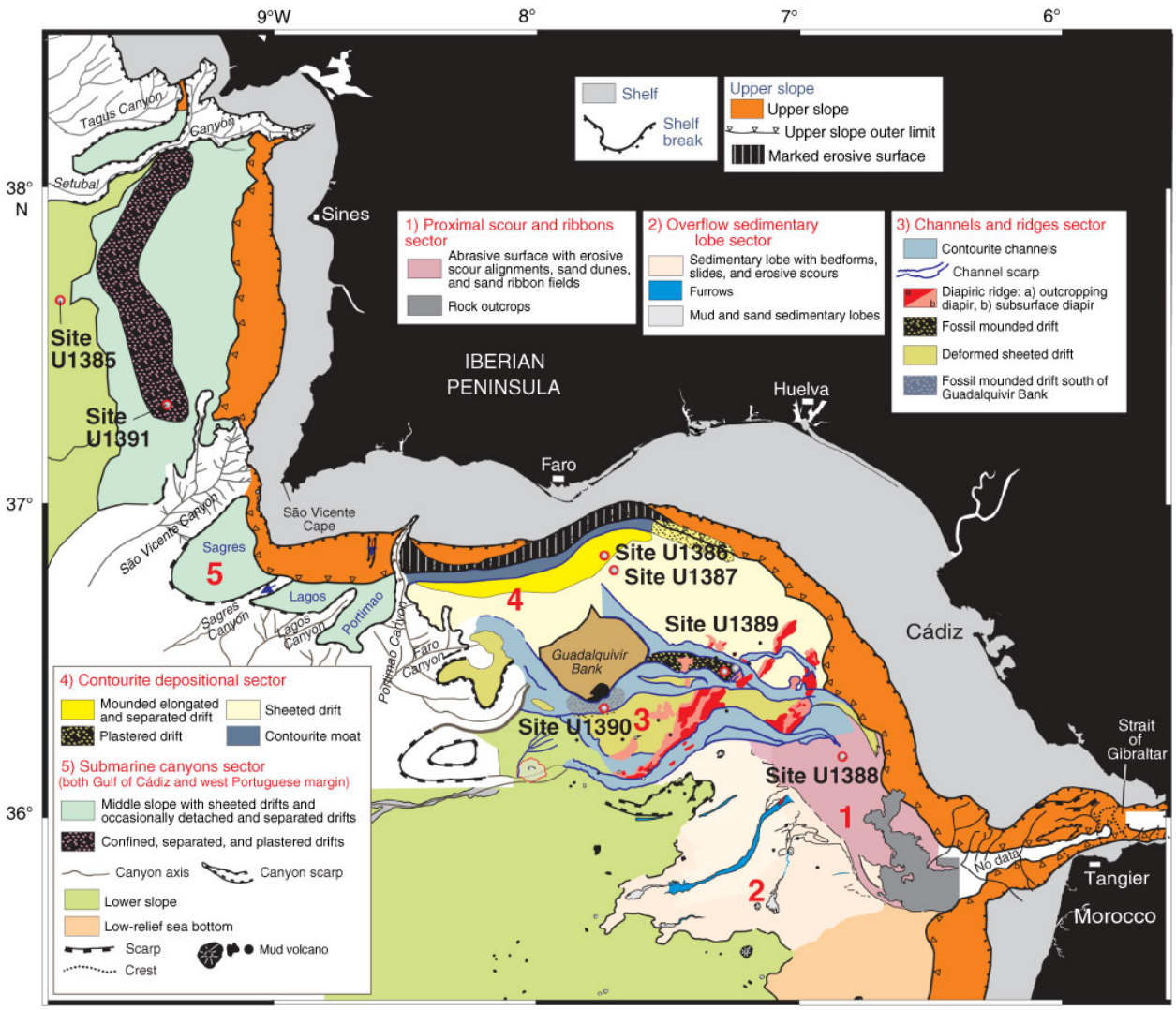

Figure 1: Expedition 339 site locations and map of the contourite depositional system (Hernandez-Molina et al., 2013).

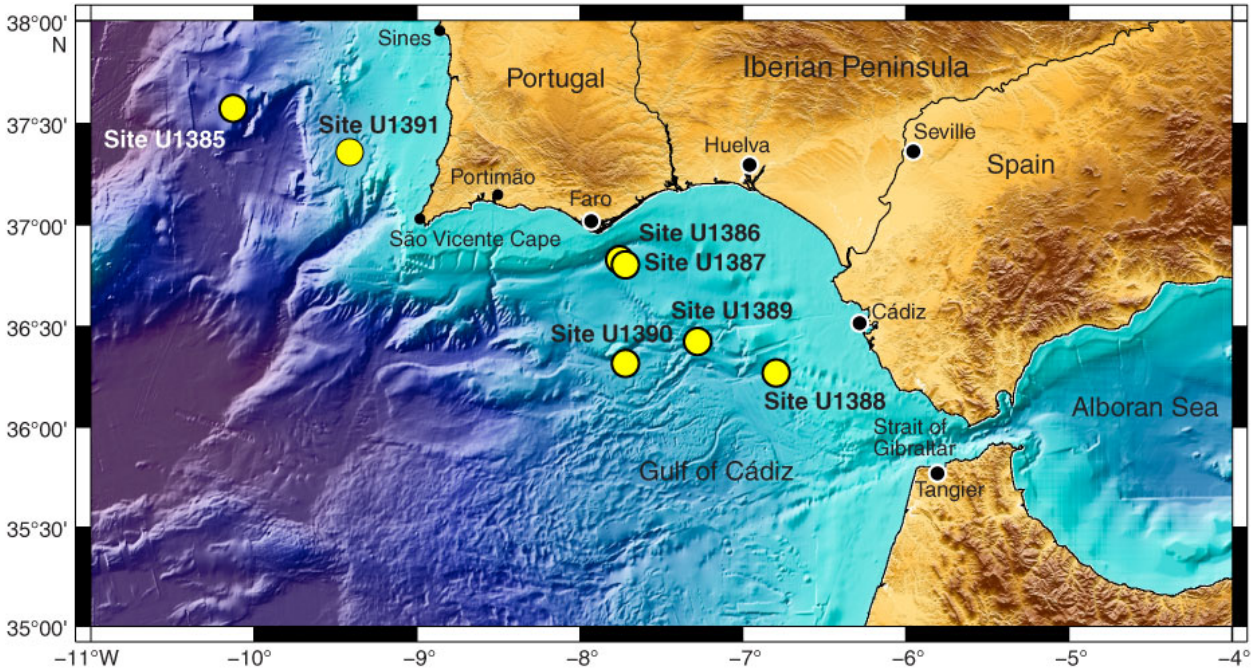

Figure 2: Expedition 339 sites in the Gulf of Cádiz and West Iberian margin (Expedition 339 Scientists, 2013a).

These deposits developed directly from the MOW and show a well-layered internal structure with laterally extensive aggradational to progradational depositional units and widespread discontinuities. These deposits also allowed scientists to conduct high-resolution examination of past environmental changes (Expedition 339 Scientists, 2013a).

Site U1389 was drilled on the southern Iberian margin, offshore the Spanish city of Cadiz (Figure 2). This site sits on top of a topographic high and is in the channels and ridges sector of the Cadiz CDS. The area is a small remnant of a middle-slope sheeted drift system that originally was more extensive, but has been eroded by several

contourite channels. Site U1389 showed a well-layered internal structure with laterally extensive, aggradational depositional units and widespread discontinuities (Expedition 339 Scientists, 2013a).

Multiple students at The Ohio State University have also been studying composition of the Gulf of Cadiz sediments and the history of the Mediterranean Outflow Water. Two students in particular, Amber Huston (Huston, 2015) and Erin Lathrop (Lathrop, 2015) produced mineral composition data similar to the shipboard data used here. Their goals included defining mineral abundances during glacial and interglacial periods, and identifying the causes of any mineral variations observed.

Huston (2015) defined covarying mineral assemblages at Site U1387 for Pleistocene aged sediment and attempted to identify compositional changes during glacial and interglacial cycles. She determined that quartz and dolomite covaried, and that illite and 7Å clays covaried. She determined that calcite did not covary with any other minerals, and was unable to identify a definite pattern of mineral abundance variations during glacial and interglacial cycles. She attributed the covariation of quartz/dolomite vs. illite/7Å clays to changes in overall sediment grain size (Huston, 2015).

Lathrop (2015) identified primary mineral phases of quartz, calcite, dolomite, aragonite, illite, 7Å clay, and other interstratified clays in Pleistocene aged sediment

from Sites U1387 and U1389. She interpreted a local provenance and explained mineral variations by changes in weathering and in sediment transport paths. Lathrop (2015) also was unable to identify any consistent variations in mineral abundances between glacial and interglacial periods, and concluded that multiple controls influence the contourite depositional system in the Gulf of Cadiz (Lathrop, 2015).

The covarying mineral assemblages described by Huston (2015) and Lathrop (2015) were defined by visual examination of abundance plots downcore at their respective IODP sites. An alternative and statistically more robust approach is to use Principal Component Analysis, or Factor Analysis, to establish associations among minerals. After mineral assemblages have been established, those assemblages can be used to interpret sediment maturity and sediment source areas. For example, Achab and Gutierrez (2009) used factor analysis to determine heavy mineral associations in the Bay of Cadiz. The factor analysis results established mineral associations among zircon, hornblende, andalusite, garnet, topaz, tourmaline, and rutile, which could then be traced back to sources adjacent to the study area. Achab and Gutierrez (2009) were able to determine the sediment transport method for these mineral assemblages using the factor analysis results. The work presented herein, along with others using sediment mineralogy and geochemistry over the past 40 years confirms that principal component analysis is a very useful tool when determining provenance of sediment in an area.

Methods

X-ray diffraction (XRD) analysis was done onboard the JOIDES Resolution during Expedition 339, using a Bruker D-4 Endeavor diffractometer mounted with a Vantec-1 detector and using nickel-filtered CuKα radiation. The voltage used was 37 kV, with a current of 40 mA. Eighty-nine samples from Site U1387 and 98 samples from Site U1389 were analyzed. One 5 cm^3 sample was taken per core (around one sample every 10 m), and the samples were ground by hand or in an agate ball mill. Samples were scanned over a range of 4°–70°2θ, with a divergence slit of 0.3mm, step size of 0.0174°2θ, and a scan speed of 1 s/step (Expedition 339 Scientists, 2013b).

The most common mineralogical components present and their relative abundances were given by the XRD analysis. In order to identify minerals and peak characteristics, the EVA software package was used to evaluate diffractograms of bulk samples. For each mineral identified, peak intensities were documented to show how each mineral varied between sites and downhole (Expedition 339 Scientists, 2013b).

In order to calibrate the bulk XRD intensities, the peak intensities had to be compared to independent measurements of the same material. Therefore XRD results and $CaCO_3$ determinations were made on the samples, and percent $CaCO_3$ was compared with peak intensities of calcite and dolomite. The resultant data showed a

good correlation between the intensity of a particular XRD peak and the amount of that material in a sediment sample (Expedition 339 Scientists, 2013b).

In order to obtain high quality data for the clays, the clay minerals had to be separated from coarser sediments and scanned separately as oriented samples. The clay fraction was separated by centrifuging. The clay minerals were scanned twice; once before an ethylene glycol treatment, and then again after that treatment. This pair of analyses allowed additional evaluation of the clay mineral fraction (Expedition 339 Scientists, 2013b).

The data analysis for this project was done using PAST software, version 3.06, downloaded from http://folk.uio.no/ohammer/past/. After downloading PAST, Excel files with the shipboard XRD peak intensities for Site U1387 and U1389 were copied and pasted into the PAST software. The Site U1387 Excel data file can be found at http://publications.iodp.org/proceedings/339/105/105_t4.htm, and the Site U1389 data file can be found at http://publications.iodp.org/proceedings/339/107/107_t6.htm. When working within PAST, the column attributes and the row attributes boxes were checked, and column 1 was copied and pasted into the "name" column, and the "core, section" row was copied and pasted into the "name" row. The boxes were then unchecked and renaming the rows and columns was completed. Next the "core, section" through "339-"columns were removed and the "NAs" found throughout the

Excel file were replaced by zeroes. The “Quartz” through “Aragonite” rows were then all selected and run through the principal components analysis. The data analysis was run by clicking on “Multivariate” → “Ordination” → “Principal Components (PCA).”

Results

For Site U1387, the principal component analysis defines 13 factors that explain 100% of the original data variance (Table 1). However only the first three are considered important and those three together explain approximately 57% of the total data variance (Figures 3-6). Principal Component 1 accounts for approximately 22% of the variance, and is defined by high positive values for plagioclase, dolomite, and kaolinite (Figure 3) vs. high negative values for K-feldspar, augite, and chlorite. As a result, Principal Component 1 identifies two distinct mineral assemblages. Principal Component 2 accounts for approximately 18% of the total variance, and is defined by high positive values for K-feldspar, kaolinite, augite and pyrite (Figure 4) vs. high negative values for chlorite and aragonite. For the purposes of this study pyrite will be ignored in the discussion of the mineral assemblages because pyrite is diagenetic, rather than detrital. Chlorite is the only variable with a high positive value for Principal Component 3, which accounts for approximately 15% of the variance (Figure 5). There is no equivalent high negative value for Principal Component 3. Table 2 shows the loadings data for all 13 of the principal components, and the SCREE plot, which is a simple plot of eigenvalues, is shown in Figure 6.

Table 1: Site U1387 Data Summary Table.

PC	Eigenvalue	% variance
1	170981	22.506
2	139813	18.404
3	120772	15.897
4	79152.1	10.419
5	70698.1	9.3061
6	58843.5	7.7456
7	45956.2	6.0493
8	28412.4	3.74
9	24086.4	3.1705
10	12775.4	1.6816
11	8086.54	1.0644
12	94.8895	0.01249
13	27.2288	0.0035842

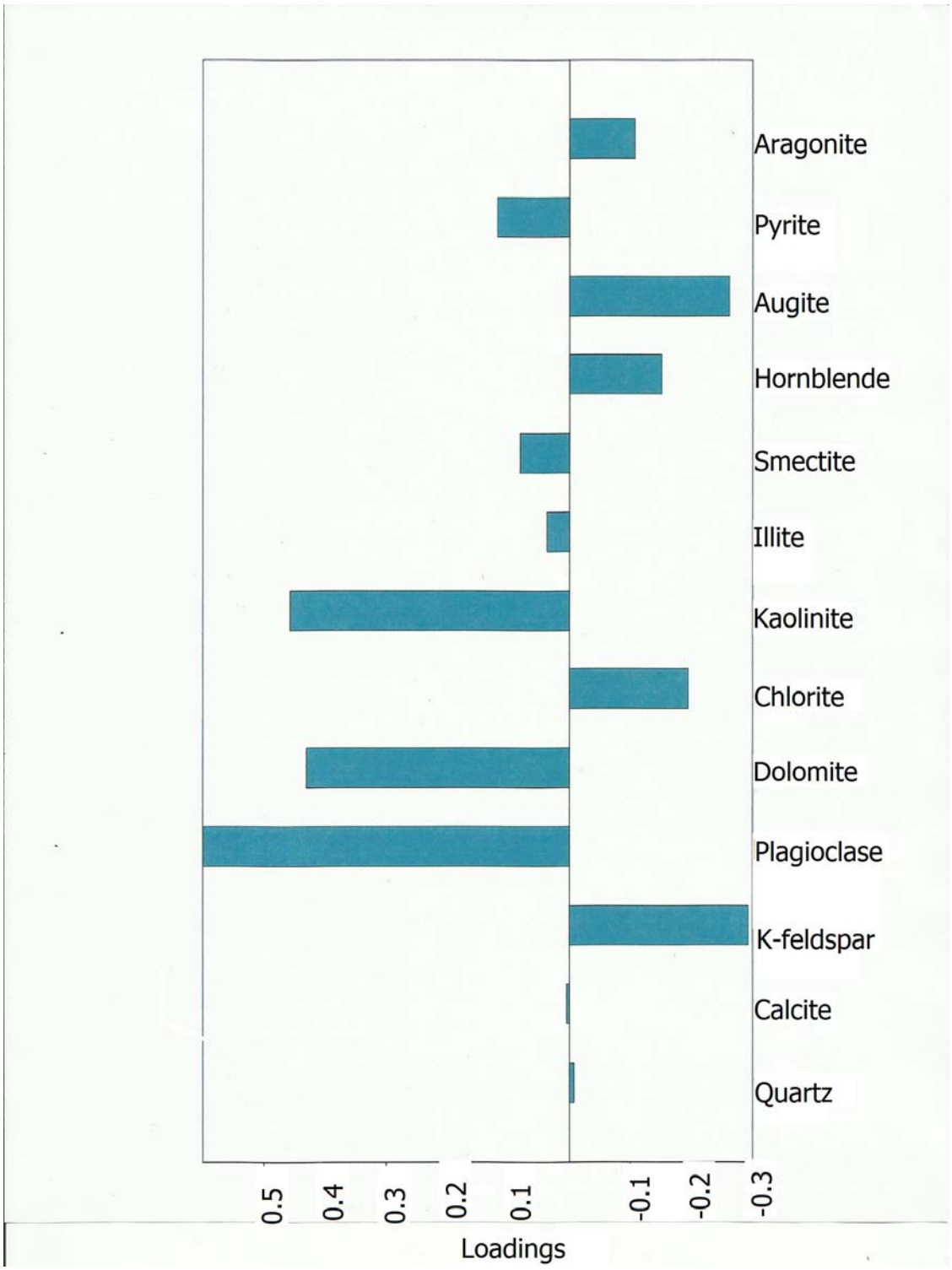

Figure 3: Principal Component One Loadings Plot at Site U1387.

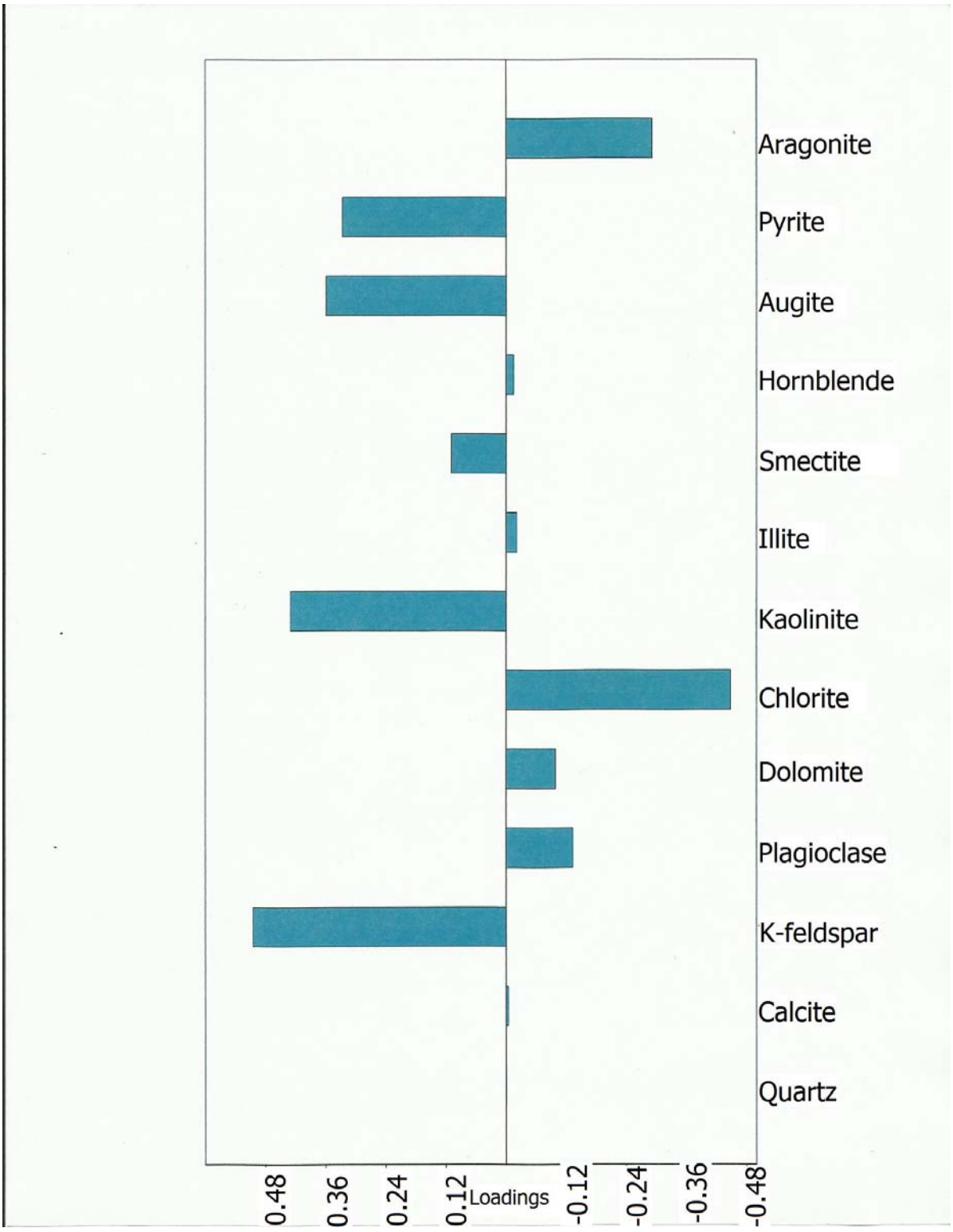

Figure 4: Principal Component Two Loadings Plot at Site U1387.

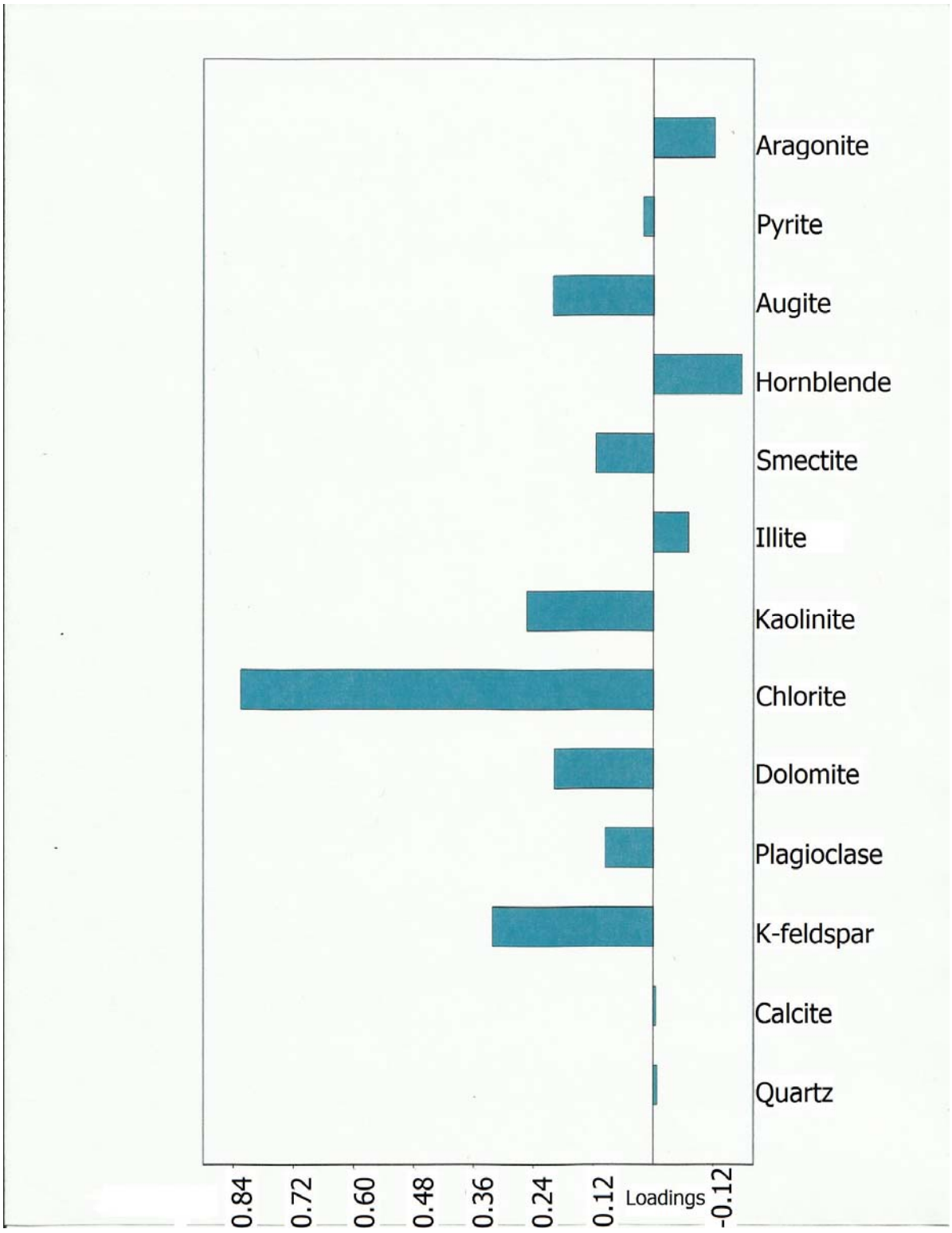

Figure 5: Principal Component Three Loadings Plot at Site U1387.

Table 2: Loadings Data for Site U1387.

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
Quartz	-0.00758	-0.00046	-0.00698	0.002961	0.001079	0.008672
Calcite	0.004064	-0.00441	-0.00418	0.000514	0.002124	-0.00295
K-feldspar	-0.29225	0.50441	0.32123	-0.4737	0.41526	0.3523
Plagioclase	0.59877	-0.1331	0.095598	-0.40627	-0.2095	0.16558
Dolomite	0.43039	-0.09836	0.19786	-0.173	-0.02794	0.045501
Chlorite	-0.1942	-0.44772	0.8247	0.1198	0.008005	-0.13762
Kaolinite	0.45695	0.43003	0.25266	0.60409	0.11093	0.2989
Illite	0.036034	-0.02093	-0.06983	-0.02392	-0.03712	0.056432
Smectite	0.080476	0.10938	0.11524	-0.09188	0.22101	-0.26445
Hornblende	-0.15099	-0.01515	-0.17557	-0.00565	-0.10306	0.14232
Augite	-0.26151	0.35897	0.20073	0.14024	-0.74301	0.06707
Pyrite	0.11752	0.32627	0.019816	0.11401	0.18071	-0.73124
Aragonite	-0.10711	-0.29126	-0.12178	0.39953	0.35348	0.32474

	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13
Quartz	-0.00507	-0.01085	-0.00111	0.018522	-0.03133	0.75073	-0.65935
Calcite	-0.00044	-0.00957	0.005784	-0.00628	-0.03681	0.65854	0.75149
K-feldspar	0.038414	0.10683	0.14873	0.030467	-0.00804	0.002597	0.004686
Plagioclase	0.56058	0.22701	-0.01104	0.10678	-0.02994	0.006034	-0.00453
Dolomite	-0.78419	0.30269	0.15766	0.004043	0.041043	0.005485	-0.00201
Chlorite	0.1062	-0.08558	0.052514	0.1336	0.095326	0.007168	0.000437
Kaolinite	0.040249	-0.2388	-0.05767	0.10537	0.052702	1.52E-05	0.002783
Illite	0.087927	-0.10777	0.36351	-0.38144	0.83043	0.040587	-0.00256
Smectite	-0.01991	0.18427	-0.81301	-0.2071	0.31972	0.024835	3.73E-06
Hornblende	-0.07397	0.096929	-0.13162	0.83181	0.43654	0.011931	0.020688
Augite	0.003099	0.39704	-0.05582	-0.1591	0.005586	0.010722	0.00194
Pyrite	0.15417	0.32293	0.36094	0.19988	0.024854	0.007697	-0.0045
Aragonite	0.13792	0.68116	0.054344	-0.11294	-0.00983	0.005358	0.000407

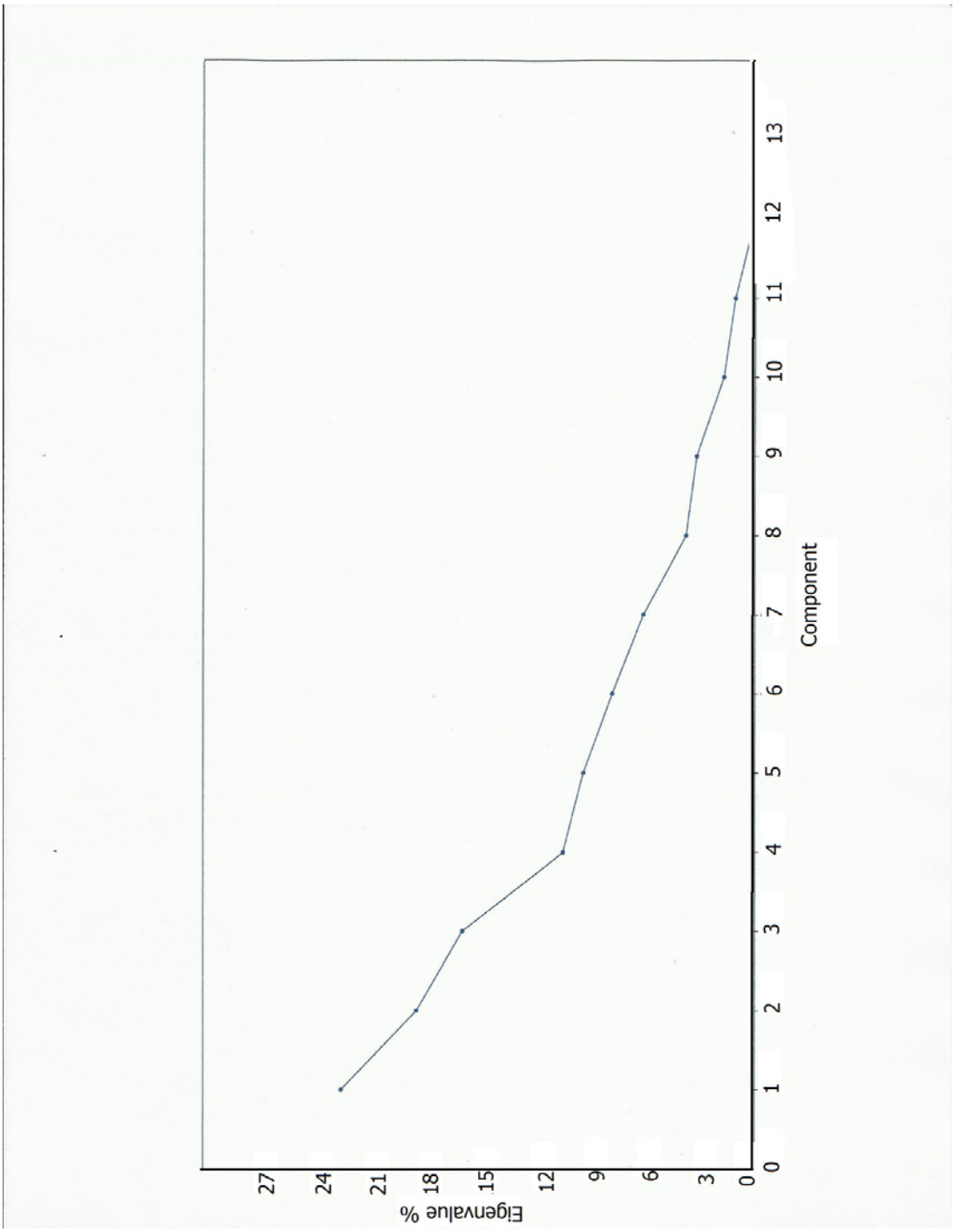

Figure 6: Site U1387 SCREE Plot.

For Site U1389, the principal components analysis also defined 13 components that explain 100% of the data variance (Table 3), but only the first three are considered important. Those three components account for approximately 62% of the total data variance (Figures 7-10). Principal Component 1 is defined by high positive values for plagioclase, dolomite, and chlorite, and explains approximately 30% of the original total variance (Figure 7). Aragonite has a moderately negative loading, and varies inversely with the three minerals with high positive loadings on Principal Component 1. Two minerals, plagioclase and dolomite, have moderate positive loadings on Principal Component 2 which accounts for approximately 17% of the total data variance (Figure 8). Chlorite has a high negative loading on Principal Component 2. Principal Component 3 explains 13% of the total variance (Figure 9), and is defined by a high positive loading on aragonite and a moderate negative loading on K-feldspar. The loadings data for Site U1389 are shown in Table 4, and Figure 10 shows the corresponding SCREE plot.

Table 3: Site U1389 Data Summary Table.

Principal Component	Eigenvalue	% variance
1	221449	29.871
2	125244	16.894
3	113691	15.336
4	77378.8	10.438
5	70428.6	9.5001
6	54130.9	7.3017
7	36452.8	4.9171
8	22117.8	2.9835
9	13339.8	1.7994
10	7068.71	0.95349
11	40.5525	0.0054701
12	4.21393	0.00056841
13	2.79809	0.00037743

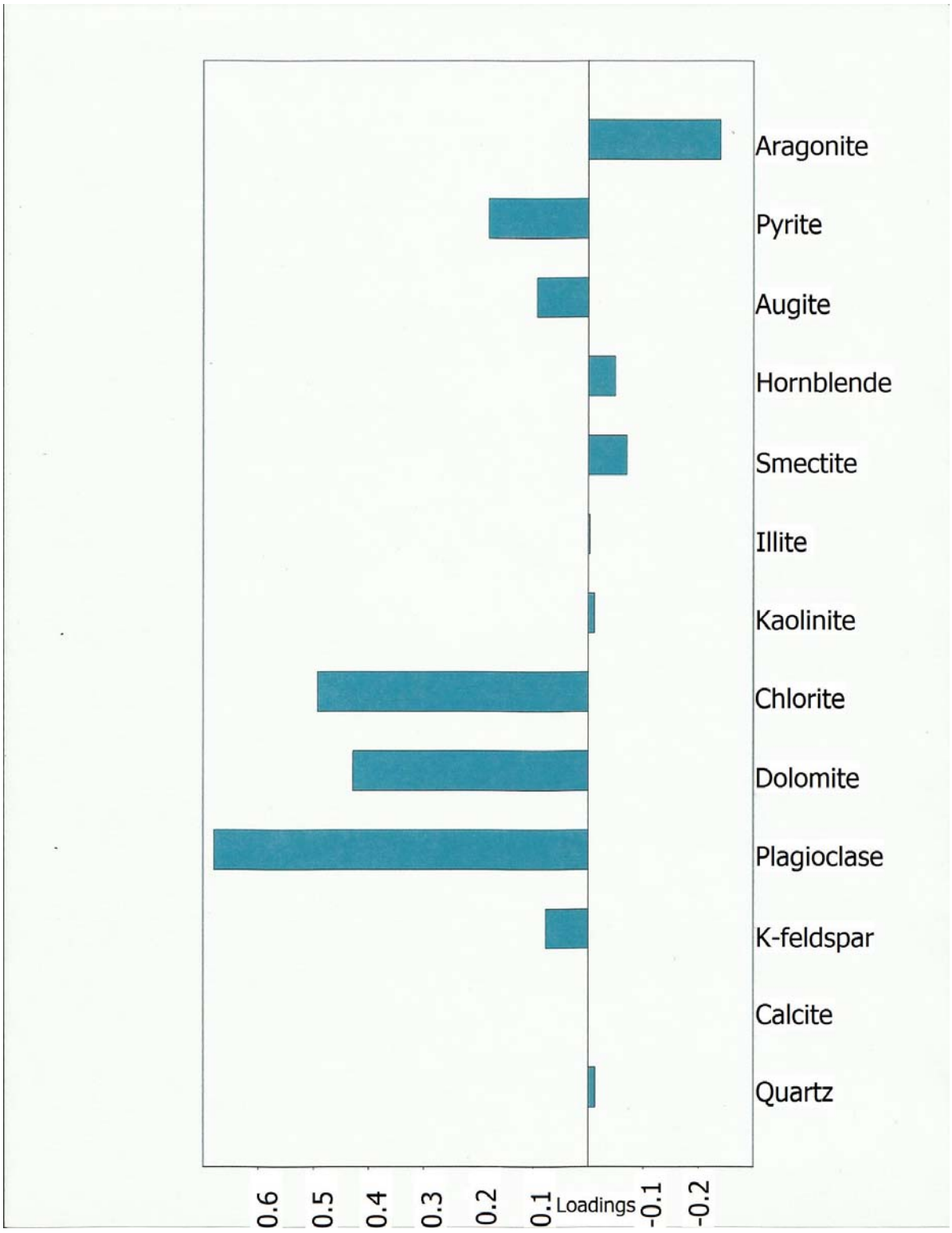

Figure 7: Site U1389 Loadings Plot for Principal Component One.

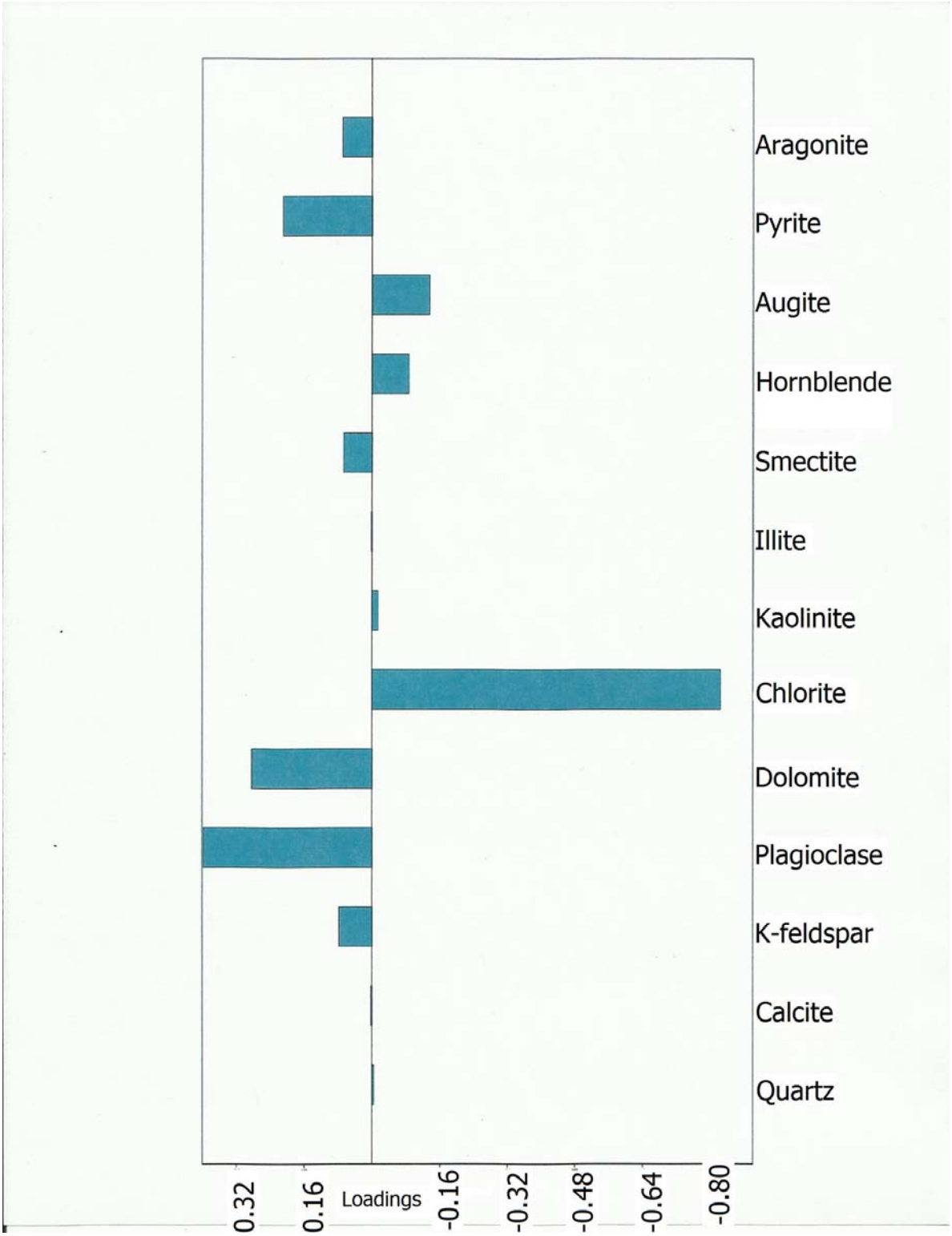

Figure 8: Principal Component Two Loadings Plot at Site U1389.

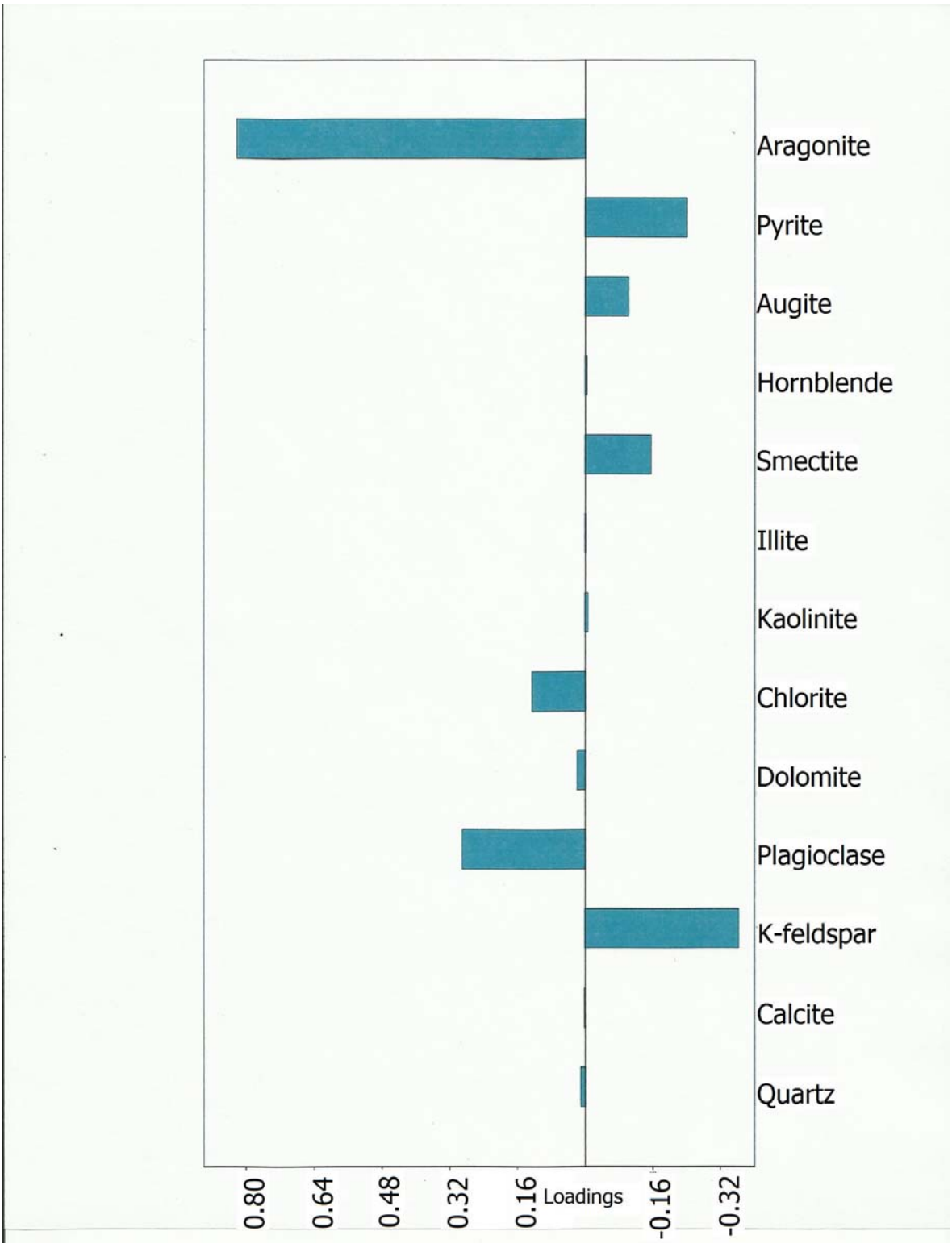

Figure 9: Site U1389 Loadings Plot for Principal Component Three.

Table 4: Loadings Data for Site U1389.

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
Quartz	-0.01214	-0.00353	0.009622	-0.00093	-0.00157	0.005174
Calcite	-0.00028	0.002172	0.001424	-6.37E-05	-0.00119	0.001717
K-feldspar	0.076763	0.076835	-0.36179	0.90063	-0.00052	-0.17492
Plagioclase	0.68004	0.3971	0.29044	-0.0628	-0.15145	-0.48029
Dolomite	0.42785	0.28233	0.018058	0.091191	0.13213	0.60871
Chlorite	0.49235	-0.82323	0.12509	0.10373	-0.07611	0.15045
Kaolinite	-0.01085	-0.01333	-0.00609	-0.0558	-0.02378	0.003901
Illite	-0.00235	0.001285	-0.00116	-6.71E-05	-0.00019	0.00031
Smectite	-0.06931	0.066427	-0.1554	0.017324	-0.06194	0.070149
Hornblende	-0.0483	-0.08635	-0.00346	0.10446	-0.00994	-0.01652
Augite	0.092672	-0.13534	-0.1017	-0.0926	0.8872	-0.35372
Pyrite	0.18102	0.20941	-0.23978	-0.07453	0.3146	0.43779
Aragonite	-0.23962	0.069012	0.82259	0.37065	0.25141	0.15343

	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13
Quartz	-0.00543	0.015843	-0.00311	0.012605	0.99875	0.031229	-0.02823
Calcite	-0.00145	0.002546	-0.00042	-0.00088	-0.0321	0.99908	-0.02825
K-feldspar	0.034514	-0.04705	-0.10821	-0.02007	0.007254	0.001073	0.000227
Plagioclase	0.15988	0.057377	0.060859	0.072913	0.008311	1.99E-05	0.000804
Dolomite	-0.57359	-0.08075	0.064679	0.029764	0.001223	-0.00192	0.000411
Chlorite	0.13853	-0.06122	0.031895	0.032897	0.002478	0.001952	0.002359
Kaolinite	-0.05424	-0.0083	-0.62576	0.7754	-0.01206	3.04E-05	0.002238
Illite	-0.00036	0.004599	0.004036	0.000788	0.027239	0.029118	0.99918
Smectite	0.19888	-0.38785	0.67799	0.5549	0.002668	0.001948	-0.00191
Hornblende	-0.15462	0.87968	0.32923	0.26913	-0.01792	-0.00261	-0.00508
Augite	-0.16482	-0.07072	0.07259	0.066863	0.004311	0.0023	0.000285
Pyrite	0.70821	0.23003	-0.11779	-0.03666	0.003685	1.46E-05	-0.0006
Aragonite	0.17291	-0.04138	0.024165	0.068902	-0.00979	-0.0012	0.000735

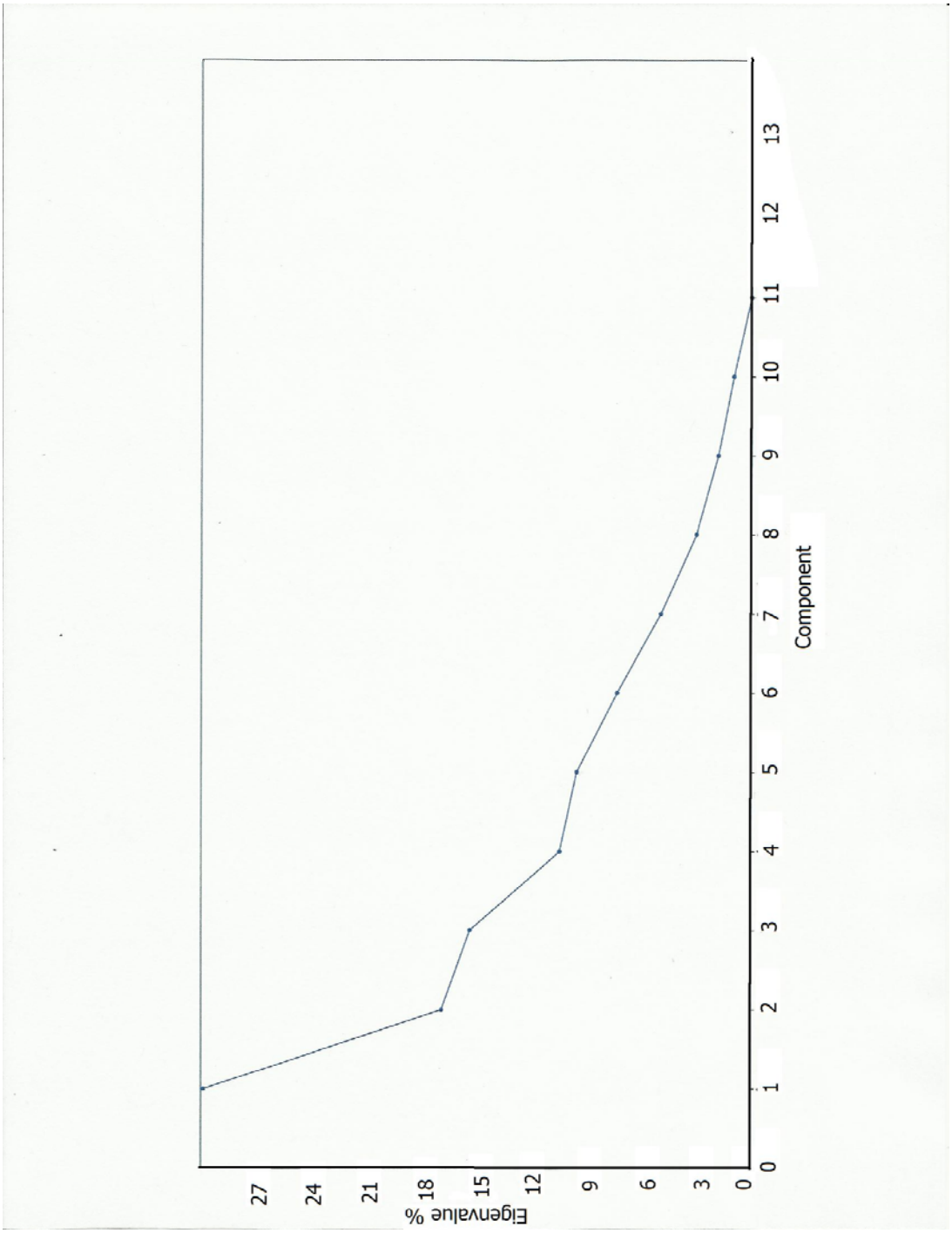

Figure 10: SCREE Plot for Site U1389.

Discussion

The principal component analysis of mineral abundances at Site U1387 identified three important principal components, and five mineral assemblages, that explain 57% of the data variance. The first principal component, which accounts for 22% of the data variance, is defined by an association of plagioclase, dolomite and kaolinite that varies inversely with an association of K-feldspar, augite and chlorite. The most likely causes for these covarying associations, and for the inverse relationship between these two associations, are variations in weathering or in the sediment source area. In the case of weathering, plagioclase, dolomite, and kaolinite may have been provided from a source area (or during a time) experiencing more extensive chemical weathering than the conditions that supplied K-feldspar, augite, and chlorite. Site U1387 is near the Guadiana River (Figure 11), which could have transported the sediment that contains plagioclase, dolomite, and kaolinite. Found within the Guadiana River basin are Rana deposits, which originate as alluvial platforms. These deposits are generally thin, clast-supported siliciclastic conglomerates of fluvial origin. They are typically strongly weathered with partially disintegrated pebbles and intense alteration of the argillaceous material (Gibbons and Moreno, 2002).

Figure 11: Map of Spain showing the Guadian and Guadalquivir Rivers

There are two possible options for the source of the K-feldspar, augite, and chlorite: 1) either the sediment supplied from the Guadiana River changed between the two assemblages above through time (either due to weathering changes within the basin, or changes in precipitation that supplied more sediment from one part of the basin at one time and from another part of the basin at another time, or 2) sediment from another source region was transported in episodically.

Principal Component 2 explains 18% of the data variance, and is defined by a mineral assemblage of K-feldspar, kaolinite, augite and pyrite. Pyrite will be ignored for the purpose of this study because it was most likely diagenetic, rather than detrital. Chlorite and aragonite are also defined as an assemblage in Principal Component 2, varying inversely with the K-feldspar, kaolinite and augite assemblage. Kaolinite is produced by fairly extensive weathering of silicic rocks, so the mineral association of K-

feldspar, kaolinite and augite is thought to originate from the Rana deposits found in the Guadiana River. However, chlorite is generally derived from more basic source rocks that have undergone limited weathering, whereas the aragonite may be either detrital or from marine biogenic sources like forams and or nannofossils. If the aragonite is mostly biogenic, then the K-feldspar, kaolinite and augite assemblage indicates terrigenous detrital input, and the aragonite and chlorite assemblage indicates more biogenic influences. However, if the aragonite is detrital, then this may be a signal of more weathering (K-feldspar, kaolinite and augite) vs. less weathering (aragonite and chlorite).

Chlorite is the only mineral associated with Principal Component 3, which accounts for 15% of the data variance. There is no mineral that inversely varies with chlorite. Chlorite is viewed as a mineral formed in terrestrial settings with mafic rocks and little chemical weathering. So Principal Component 3 may be indicating more chemical weathering (where Principal Component 3 is less important) vs. less chemical weathering (where Principal Component 3 is important).

The principal component analysis of mineral abundances of Site U1389 identified three important principal components, and six accompanying mineral assemblages, that account for 62% of the data variance. Principal Component 1 accounts for 30% of the data variance and is defined by plagioclase, dolomite and chlorite that varies inversely

with aragonite. Plagioclase, dolomite and chlorite are all terrigenous materials. This association of minerals appears to represent detrital sediments supplied to the Gulf of Cadiz, possibly from the adjacent Guadalquivir River. The aragonite identified by Principal Component 1 is biogenic and came from the marine plankton in the area. The Guadalquivir River basin is a foreland basin, and foreland basins often contain terrigenous and marine sediment. As a result, Principal Component 1 at Site U1389 appears to distinguish detrital terringenous vs. marine biogenic sediment supplied from the Guadalquivir River.

Principal Component 2 at Site U1389 accounts for 17% of the data variance, and is dominated by the importance of chlorite. However, plagioclase and dolomite also define a less important assemblage in Principal Component 2 that varies inversely relative to chlorite. The covarying of plagioclase and dolomite vs. chlorite identified by Principal Component 2 can be attributed to two potential causes. These minerals could have been supplied from slightly more weathered source than the chlorite, or deposition could have been influenced by differences in grain size. The plagioclase and dolomite may have been deposited during times of stronger bottom currents, which concentrated the larger grain sizes, whereas the chlorite may have been deposited during times of weaker currents, when the transport and deposition of smaller grains was favored.

The remaining 15% of variance is explained by Principal Component 3 which is dominated by the importance of aragonite accompanied by a weaker inverse association with K-feldspar. The aragonite is likely supplied by marine biogenic sources, whereas the K-feldspar is detrital, so Principal Component 3 at Site U1389 also appears to distinguish detrital terrigenous vs. marine biogenic sediment supplied by the Guadalquivir River.

The most straightforward interpretations of these results are for Principal Component 2 at Site U1387 and Principal Component 1 and 3 at Site U1389; in all three cases, aragonite is identified as inversely associated with one or several detrital minerals. Because much of the aragonite is likely to have a marine biogenic origin, the relationships identified by these three principal components appear to distinguish detrital terrigenous vs. marine biogenic sediment supply. The other principal components identify various assemblages of detrital terrigenous minerals, whose provenance is difficult to interpret unequivocally. The associations of minerals identified at Site U1387 and U1389 are not consistent, and some assemblages contain minerals that provide contradictory evidence about source rock type or weathering intensity. Sediment supply could have been variable over time, and additional sources besides the two rivers noted above may have supplied sediment. Some sediment could have been supplied by erosion of exposed cliffs and beaches in the area, and other

sediment could have been supplied by wind. In addition, weathering patterns could have varied within individual drainage basins, so that the sediment supplied from that basin was not homogenous at a particular time. In summary, the Gulf of Cadiz is a very complicated and diverse basin influenced by many environmental and geological factors, and the mineral composition of its sedimentary record reflects this complexity.

Suggestions for Future Research

In order to further test the hypothesis of sediment provenance from the Guadiana and Guadalquivir Rivers it would be beneficial to compare the results of other studies of the same area. Performing principal components analysis on the data of Huston (2015) and Lathrop (2015) might provide additional insight in the question of sediment provenance.

It also would be advantageous to compare the mineralogy of the offshore sediments more directly to the composition of sediment from the rivers that empty into the Gulf of Cadiz and the nearby cliffs and beaches. If the composition of nearby sediment sources was similar to the compositions found in this study, then there would be stronger evidence for the detailed local sources of the offshore mineral assemblages.

Analysis of other sites near U1387 and U1389 would help to understand the Gulf of Cadiz system overall. It would give more insight to mineral associations across the region and could identify the sources of sediment found in the Gulf of Cadiz. This could also help identify current patterns that could be related to the Mediterranean Outflow Water.

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